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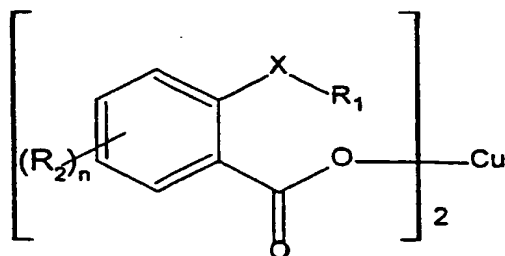
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(54) Title: COMPOSITIONS BASED ON CUPRIC SALTS, CUPRIC SALTS AND THEIR USE FOR CONTROLLING PHYTOPATHOGENS



(I)

(57) Abstract: Fungicidal compositions are described, containing one or more salts of derivatives of salicylic acid having formula (I): in any molar ratio, with at least one fungicidal compound not corresponding to a salt of derivatives of salicylic acid having formula (I).

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COMPOSITIONS BASED ON CUPRIC SALTS, CUPRIC SALTS AND
THEIR USE FOR CONTROLLING PHYTOPATHOGENS

The present invention relates to compositions based
10 on cupric salts for controlling phytopathogens.

The present invention also relates to cupric salts
of derivatives of salicylic acid and their application
for the control of phytopathogens.

Salicylic acid is a compound naturally present in
15 many vegetables. It is definitely present in extracts of
willow bark, used since antiquity as an anti-inflammatory
remedy.

Nowadays, salicylic acid is conveniently synthesized
on an industrial scale by the condensation of a phenolic
20 salt with carbon dioxide. Many of its derivatives can be
easily prepared by exploiting the particular reactivities
of the phenolic ring, of the carboxylic group and pheno-
lic hydroxyl. In particular, acetylsalicylic acid is uni-
versally known as a pharmaceutical product.

25 It has been demonstrated that salicylic acid is ca-

pable of controlling various phytopathogens through the precocious induction of defense systems naturally present in plants, but activated after infection. The presence of phytopathogens, in fact, causes a series of biochemical signals, among which an accumulation of salicylic acid in the vegetable tissues, which lead, for example, to the synthesis of specific proteins with a fungicidal activity.

It has been shown that an increase in the level of salicylic acid induced previous to fungal infections, causes a much more effective fungicidal response on the part of the plant itself (THE PLANT CELL, Vol. 8 (1996) pages 1809-1819).

To enable a fungicide to be economically acceptable in agronomic practice, it is essential for it to ensure a reliable and prolonged fungicidal action. The use of salicylic acid as such has been described as providing lower protective levels than those of other classical fungicides. For example, it is said that the control of grape mildew by the use of salicylic acid as such, is much lower than that obtained by the use of traditional cupric products.

The applicant has now found that cupric salts of some derivatives of salicylic acid are particularly convenient, with respect to those described in the state of

the art, for controlling bacterial and fungal phytopathogens. The applicant has found, in fact, that cupric salts of some derivatives of salicylic acid, when appropriately formulated, allow a prolonged protective action to be obtained on vegetables subjected to treatment, comparable to that of full doses of traditional cupric salts.

The cupric salts of derivatives of salicylic acid, object of the present invention, are moreover more effective than the corresponding non-salified derivative of salicylic acid, or salified with a different metal, in controlling phytopathogens on vegetables or parts thereof. This activity can be attributed to a concomitant induction effect reinforced by the direct action of the cupric ion. The activity registered is, in fact, also higher than that produced using a derivative of non-salified salicylic acid mixed with a traditional cupric fungicide.

An important aspect of the use of salts, object of the present invention, derives from the fact that the defense systems of plants activated by derivatives of salicylic acid have different action mechanisms and consequently allow an immunizing response which minimizes any possible production of resistant strains.

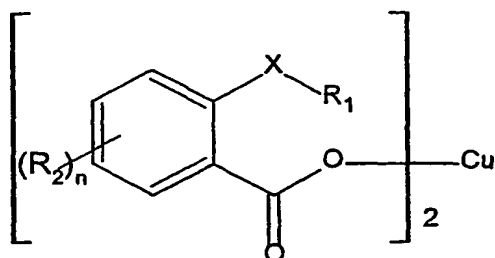
The applicant has also found that these salts form an excellent means of controlling phytopathogens also in

vegetable varieties genetically modified for amplifying the original natural defense systems or in which one or more genes have been inserted, expressing fungicidal proteins as a result of variations in the content of salicylic acid itself in the tissues.

The applicant has additionally found that the joint application of salts of derivatives of salicylic acid, object of the present invention, with other active principles gives rise to a positive synergy of biological effects, which enable an excellent control of phytopathogens even resistant to said active principles, also on vegetables which have been genetically modified.

The present invention therefore relates to the use of cupric salts of derivatives of salicylic acid mixed with other active principles for the control of phytopathogens. Furthermore, the present invention also relates to some cupric salts of derivatives of salicylic acid as such and their use for the control of phytopathogens and the cupric salts themselves.

An object of the present invention consequently relates to fungicidal compositions containing one or more salts of derivatives of salicylic acid having formula (I):



(I)

wherein:

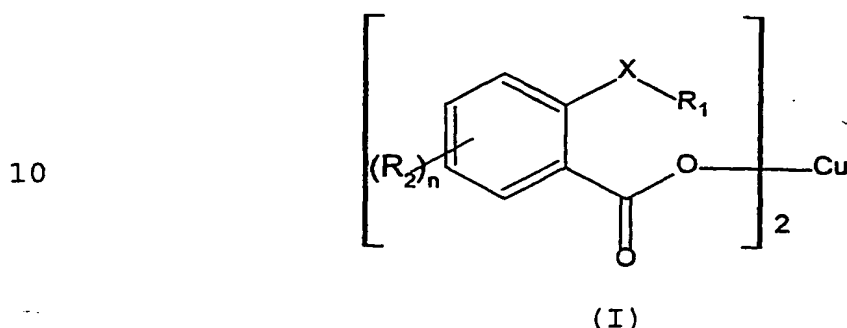
- R₁ represents H, or a CO-R' acyl group;
- R₂, the same or different when n is equal to 2, is a
 10 hydrogen, a halogen, optionally selected from fluo-
 rine, chlorine, bromine or iodine; a C₁-C₉ alkyl group;
 a C₁-C₉ haloalkyl group; a C₁-C₉ alkoxy group; a C₁-C₉
 haloalkoxy group; a C₁-C₉ thioalkyl group; a C₁-C₉ ha-
 lothioalkyl group; a C₃-C₉ cycloalkyl group; a C₂-C₁₀
 15 carboalkoxy group; a cyano group; a phenyl group; a
 hydroxyl group;
- R' represents a hydrogen; a C₁-C₉ alkyl group; a C₁-C₉
 haloalkyl group; a C₁-C₉ alkoxy group; a C₁-C₉ halo-
 alkoxy group; a C₂-C₁₀ carboalkoxy group; a phenyl
 20 group;
- n is a number ranging from 0 to 2;
- X represents an oxygen atom, a nitrogen or a sulfur
 atom;

in any molar ratio, with at least one fungicidal compound
 25 not corresponding to a salt of derivatives of salicylic

acid having formula (I).

The compounds having formula (I) can also be present in a hydrated form by the coordination of any number of water molecules.

5 A further object of the present invention relates to salts of derivatives of salicylic acid having formula (I):



wherein:

- 15 - R₁ represents H, or a CO-R' acyl group;
- R₂, the same or different when n is equal to 2, is a halogen, optionally selected from fluorine, chlorine, bromine or iodine; a C₁-C₉ alkyl group; a C₁-C₉ haloalkyl group; a C₁-C₉ haloalkoxyl group; a C₁-C₉ thioalkyl group; a C₁-C₉ halothioalkyl group; a C₃-C₉ cycloalkyl group; a C₂-C₁₀ carboalkoxyl group; a cyano group; a phenyl group; a hydroxyl group;
- 20
- R' represents an alkyl group, optionally selected from
- 25 methyl, propyl, isopropyl; or the haloalkyl group tri-

fluoromethyl; or hydrogen;

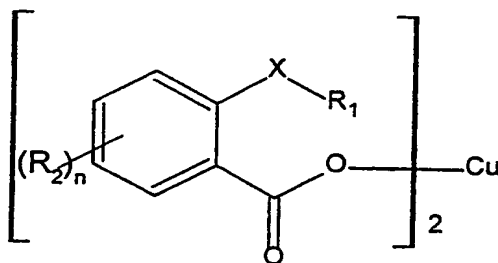
- n is a number ranging from 0 to 2;
- X represents an oxygen atom, a nitrogen or a sulfur atom;

5 with the exception, when X is equal to oxygen, of compounds wherein R_1 represents the acyl group COCH_3 and R_2 is hydrogen or chlorine and compounds wherein R_1 represents the acyl group COiPr or COEt and R_2 is hydrogen.

The compounds having formula (I) can also be present
10 in hydrated form by the coordination of any number of water molecules.

A further object of the present invention relates to the use of derivatives of salicylic acid having formula (I):

15



20

(I)

wherein:

- R_1 represents H, or a $\text{CO-R}'$ acyl group;
- R_2 , the same or different when n is equal to 2, is a halogen, optionally selected from fluorine, chlorine, bromine or iodine; a $\text{C}_1\text{-C}_9$ alkyl group; a $\text{C}_1\text{-C}_9$ haloal-

25

kyl group; a C₁-C₉ alkoxy group; a C₁-C₉ haloalkoxy group; a C₁-C₉ thioalkyl group; a C₁-C₉ halothioalkyl group; a C₃-C₉ cycloalkyl group; a C₂-C₁₀ carboalkoxy group; a cyano group; a phenyl group; a hydroxyl group;

- R' represents an alkyl group, optionally selected from methyl, propyl, isopropyl; or the haloalkyl group trifluoromethyl; or hydrogen;
- n is a number ranging from 0 to 2;
- 10 - X represents an oxygen atom, a nitrogen or a sulfur atom;

for the control of phytopathogens on vegetables or parts thereof.

The compounds having formula (I) can also be present in hydrated form by the coordination of any number of water molecules.

The compositions according to the present invention which comprise one or more salts of derivatives of salicylic acid (I) associated with at least one other fungicidal compound not corresponding to a salt of derivatives of salicylic acid having formula (I), are therefore advantageously characterized by inducing natural defense together with the direct effect of the cupric ion, forming an excellent control system of phytopathogens which exerts a synergic action with many active principles,

representing an optimum instrument for anti-resistance strategies.

In particular, the fungicidal compound not corresponding to a salt of derivatives of salicylic acid having formula (I) can be selected from inhibitors of ergosterol biosynthesis, inhibitors of mitochondrial respiration, acylanilines, systemic anti-mildew fungicides, a dipeptide with a fungicidal activity, cytotropic anti-mildew fungicides, contact fungicides, cupric fungicides, inhibitor fungicides of melanin biosynthesis.

A fungicidal compound not corresponding to a salt of derivatives of salicylic acid having formula (I) is preferably selected from tetraconazole, difenoconazole, myclobutanil, flusilazole, epoxyconazole, fenpropimorf, fenpropidin, azoxystrobin, kresoxym methyl, trifloxystrobin, metalaxyl, benalaxyl in its racemic form or as an optically active R isomer (called IR 6141), iprovalicarb, ethaboxam, cyazofamid, cymoxanil, mancozeb, clorotalonil, folpet, ditianon, copper hydroxide, copper oxychloride, cuprocalcium oxychloride.

For these preferred compositions, as can be observed in the experimental examples, an extremely important synergic effect has been identified.

In the above formulae, C₁-C₉ alkyl group refers to a linear or branched C₁-C₉ alkyl group, optionally substi-

tuted by one or more substituents, the same or different from each other.

Examples of this group are: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, terbutyl.

- 5 C_1 - C_9 haloalkyl group refers to a linear or branched alkyl group substituted by one or more halogen atoms, the same or different, optionally selected from fluorine, chlorine, bromine, iodine.

Examples of this group are: fluoromethyl, difluoro-
10 romethyl, trifluoromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2,2,2-trichloroethyl, 2,2,3,3-tetrafluoropropyl, 2,2,3,3,3-pentafluoropropyl.

- C_1 - C_9 alkoxyl group refers to a C_1 - C_9 alkoxyl group, wherein the aliphatic portion is a C_1 - C_9 alkyl group, as
15 defined above.

Examples of this group are: methoxyl, ethoxyl.

C_1 - C_9 haloalkoxyl group refers to a C_1 - C_9 haloalkoxyl group, wherein the aliphatic portion is a C_1 - C_9 haloalkyl group, as defined above.

- 20 Examples of this group are: trifluoromethoxyl, 1,1,2,2-tetrafluoroethoxyl, 1,1,2,3,3,3-hexafluoroprop-
yloxyl.

- C_1 - C_9 thioalkyl group refers to a C_1 - C_9 thioalkyl group, wherein the aliphatic portion is a C_1 - C_9 alkyl
25 group, as defined above. Examples of this group are:

thiomethyl, thioethyl.

C₁-C₉ halothioalkyl group refers to a C₁-C₉ halothioalkyl group, wherein the aliphatic portion is a C₁-C₉ haloalkyl group, as defined above.

5 Examples of this group are: trifluorothiomethoxyl, 1,1,2,2-tetrafluorothioethoxyl.

C₃-C₉ cycloalkyl group refers to a cycloalkyl group whose ring consists of 3-6 carbon atoms, optionally substituted by one or more substituents, the same or different
10 ent to each other.

Examples of this group are: cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl.

C₂-C₁₀ carboalkoxyl group refers to a carboalkoxyl group, wherein the aliphatic portion is a C₁-C₉ alkyl
15 group, as defined above.

Examples of this group are: carboxymethyl, carboxyethyl, carboxypropyl.

Optionally substituted refers to one or more substituents, the same or different, selected from the following groups: halogen atoms, alkyls, alkoxy, alkylthio, cyano, hydroxy, aminocarbonyls, carboalkoxyls.
20

R₂ is preferably selected from fluorine, chlorine, methyl, trifluoromethyl, hydroxyl.

Some further examples of fungicides which can be
25 used in the compositions according to the present inven-

tion are listed below. Among others, one or more of the following fungicides can therefore be selected:

1. as inhibitors of ergosterol biosynthesis, for example, triazole, imidazole, pyrimidine and pyridine fungicides and/or derivatives of morpholine or piperidine;
5
2. as inhibitors of mitochondrial respiration, for example, analogous synthetic products of strobilurine, or fenamidone, famoxadone, ethaboxam, fluazinam or cyazofamid;
- 10 3. among acylanilines, metalaxyl or benalaxyl, in their racemic form or as optically active R isomers, oxadixyl and/or ofurace;
4. as systemic anti-mildew fungicides, iprovalicarb, dimethomorph, flumetover, the Chinese product SYP-L-
15 190, a dipeptide with a fungicidal activity, propamocarb and/or zoxamide;
5. as cytotropic anti-mildew fungicides, cymoxanil;
6. as contact fungicides, chlorothalonil, folpet, thiram, propineb, maneb, zineb, dichlofluanide, tolil-
20 fluanide, captan, folpet and/or dithianon;
7. as cupric fungicide, copper hydroxide $\text{Cu}(\text{OH})_2$, copper oxychloride $(3\text{Cu}(\text{OH})_2 \cdot \text{Cu}(\text{Cl})_2)$, cuprocalcium oxychloride $(3\text{Cu}(\text{OH})_2 \cdot \text{Ca}(\text{Cl})_2)$, and/or tribasic copper sulfate $(3\text{Cu}(\text{OH})_2 \cdot \text{Cu}(\text{SO}_4))$;
- 25 8. as inhibitor fungicide of melanin biosynthesis, tri-

cycloazole and/or carpropamid.

Examples of triazole fungicides are: tetraconazole, epoxyconazole, difenoconazole, etc.

Examples of pyrimidine fungicides are: nuarimol,
5 fenarimil, etc.

Examples of derivatives of morpholine are: fenpropimorf, fenpropidin, spiroxamina.

Examples of analogous products of strobilurine are: azoxystrobin, kresoxim methyl, pyraclostrobin, etc.

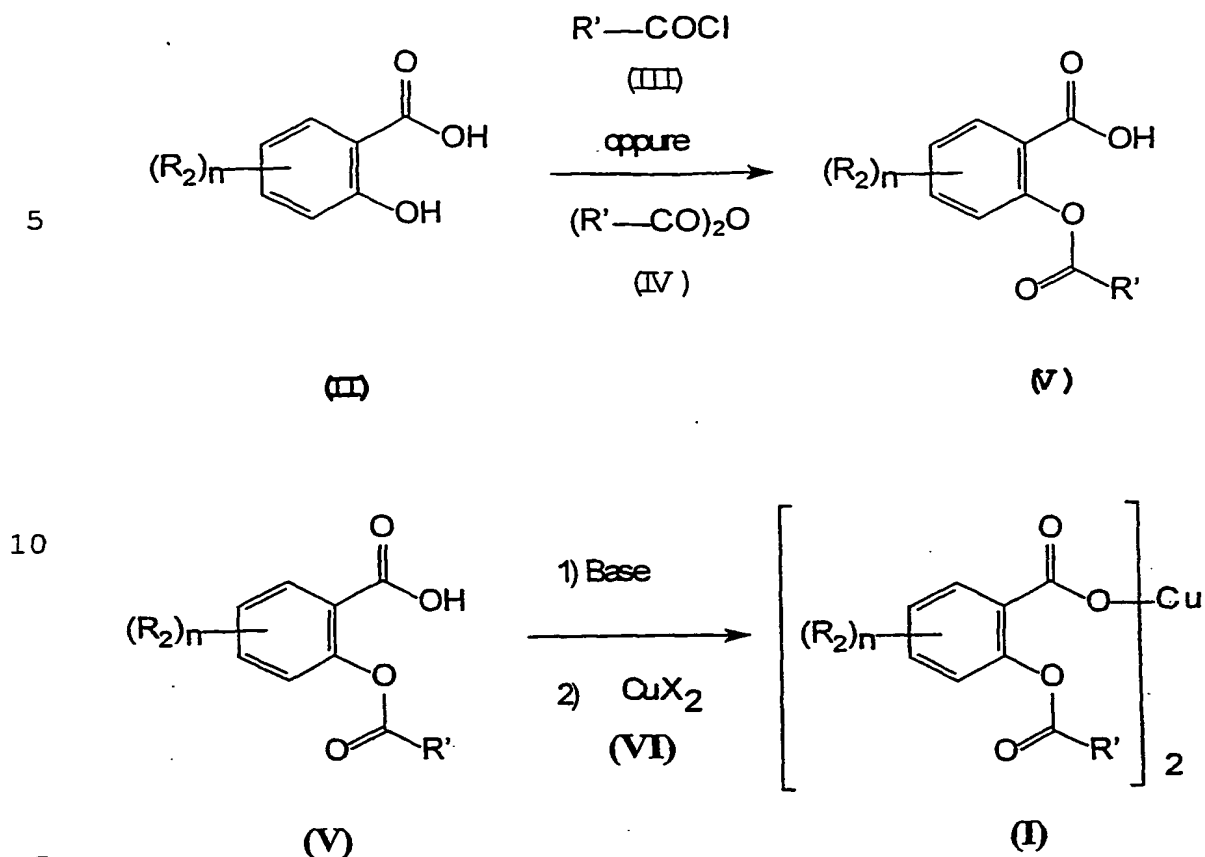
10 Fungicidal compounds not corresponding to a salt of derivatives of salicylic acid having formula (I) are commercial compounds or products about to be commercialized. Their description can be easily found in technical literature, for example in "The pesticide manual", 2000, XII
15 edition, British Crop Protection Council Ed.

Dipeptide derivative with a fungicidal activity refers to one of the compounds among those claimed in patent application EP 1028125.

The compounds having formula (I) can be easily obtained by means of numerous synthetic methods. For illustrative but non-limiting purposes, for example, the following preparation for compounds having formula (I), wherein X has the meaning of oxygen and R₁ is a -CO-R' acyl group, is provided (Scheme A):
20

25

Scheme A



The acid having formula (II) is acylated with an acyl chloride having formula (III) in an organic solvent such as dichloromethane, or 1,2-dichloroethane, or ethyl acetate in the presence of an organic base, such as pyridine or triethylamine, or inorganic, such as sodium or potassium bicarbonate, or the acid having formula (II) is acylated with the anhydride (IV) under similar conditions, or also using the same anhydride (IV) as solvent. The acid derivative having formula (V) is then dissolved in water by means of an organic base, such as sodium or

potassium bicarbonate, sodium or potassium hydroxide, and the copper salt (IV) is added to the resulting solution, wherein X can be a halogen, such as chlorine or bromine, or the sulfate ion, or perchlorate, dissolved in water, obtaining a compound having formula (I). Alternatively, it is possible to use copper hydroxide or carbonate in the presence of the acid form (V), with or without an additional base, such as an organic amine, for example triethylamine, as catalyst.

10 For the preparation of the compounds having formula (I), wherein X has the meaning of nitrogen and sulfur, the same procedure is adopted as described above, using the corresponding acids having formula (II).

The salts having formula (I) wherein R_1 has the meaning of hydrogen are analogously obtained from the compound (II) operating according to the procedure described for the transformation of the intermediate (V) into the salt (I).

The salts derivatives of salicylic acid having formula (I) alone or in compositions with at least one other active principle are capable of controlling many fungal and bacterial phytopathogens, also with a reduced sensitivity towards other fungicides.

For purely illustrative and without any limiting purposes, some examples are listed below, of phytopatho-

gens controlled by compounds having formula (I) alone or in a mixture, together with examples of possible application crops:

- Plasmopara viticola on grapes;
- 5 Peronospora tabacina on tobacco;
- Venturia inaequalis on apple-trees;
- Bremia on salads, spinach;
- Phytophthora spp. on vegetables;
- Pseudoperonospora cubensis on cucurbitaceae;
- 10 Pyricularia orizae on rice.

Both compositions containing one or more salts of derivatives of salicylic acid having formula (I), and salts of derivatives of salicylic acid having formula (I), object of the present invention, are capable of exerting a high fungicidal action of both a curative and preventive nature and additionally have a low or absence of phytotoxicity.

A further object of the present invention therefore relates to a method for controlling phytopathogen fungi in agricultural crops by the application of the compounds having formula (I) or mixtures of these associated with at least one other fungicidal compound not corresponding to a salt of derivatives of salicylic acid having formula (I).

25 More specifically, an object of the present inven-

tion relates to a method which can be applied to agricultural crops for controlling phytopathogens sensitive or tolerant to fungicides not corresponding to a salt of a derivative of salicylic acid having formula (I).

5 The quantity of compound to be applied for obtaining the desired effect can vary in relation to various factors such as, for example, the crop to be preserved, the type of pathogen, the degree of infection, the climatic conditions, the formulation adopted.

10 Doses of compound ranging from 10 g to 5 Kg per hectare generally provide sufficient control.

For practical use in agriculture, it is often convenient to adopt fungicidal compositions containing one or more compounds having general formula (I) or mixtures
15 of these with at least one fungicidal compound not corresponding to a salt having formula (I).

The application of the compositions, object of the present invention, can take place on any part of the plant, for example on the leaves, stems, branches and
20 roots or on the seeds themselves before sowing, or also on the ground in which the plant grows.

Compositions can be used, in the form of dry powders, wettable powders, emulsifiable concentrates, micro-emulsions, pastes, granulates, solutions, suspensions,
25 etc.: the selection of the type of composition depends on

the specific use.

The compositions are prepared according to the known methods, for example by diluting or dissolving the active substance with a solvent and/or solid diluent medium, optionally in the presence of surface-active agents.

Silica, kaolin, bentonite, talc, fossil flour, dolomite, calcium carbonate, magnesia, chalk, clays, synthetic silicates, attapulgite, sepiolite, can be used as solid inert diluents, or carriers.

10 In addition to water, various solvents such as aromatic solvents (xylols, mixtures of alkylbenzols); paraffins (petroleum fractions); alcohols (methanol, propanol, butanol, octanol, glycerin); amines; amides (N,N-dimethylformamide, N-methylpyrrolidone); ketones (cyclo-
15 hexanone, acetone, acetophenone, isophorone, ethylamylketone); esters (isobutyl acetate, methyl esters of fatty acids obtained for example by the transesterification of vegetable oils), can be used as liquid diluents.

Sodium, calcium, triethanolamine salts, or trieth-
20 ylamine salts of alkylsulfonates, alkylarylsulfonates, or polyethoxylated alkylphenols, or fatty alcohols condensed with ethylene oxide, or polyoxyethylated fatty acids, or polyoxyethylated esters of sorbitol, or ligninsulfonates, can be used as surface-active agents.

25 The compositions can also contain special additives

for particular purposes such as, for example, adhesion agents, such as gum arabic, polyvinyl alcohol, polyvinylpyrrolidone, polyacrylates.

In the above compositions, the concentration of active substances varies from 0.1% to 98%, preferably from 0.5% to 90%.

If desired, it is possible to also add other compatible active principles to the compositions, object of the present invention, such as phytohormones, antibiotics, herbicides, insecticides, fertilizers.

The following examples are provided for illustrative purposes only and do not limit the scope of the present invention.

EXAMPLE 1

15 Preparation of the copper salt of acetylsalicylic acid (Compound Nr. 1)

3 g of acetylsalicylic acid are added to a solution of 1.39 g of sodium bicarbonate in 15 cm³ of water. When the acid is completely dissolved, a solution of 2.07 g of cupric sulfate in 15 cm³ of water are slowly added dropwise. After 3 hours, the precipitate thus obtained is filtered and washed with hexane, obtaining, after drying in air, 3.4 g of compound Nr. 1 (yield: 48.4%). The analytical composition of compound Nr. 1 is indicated in Table 1.

EXAMPLE 2

The following compounds, whose analytical composition is indicated in Table 1, were prepared analogously to the procedure described in Example 1:

- 5 • copper salt of salicylic acid (Compound Nr. 2)
- copper salt of 5-chlorosalicylic acid (Compound Nr. 3)
- copper salt of 5-chloroacetylsalicylic acid (Compound Nr. 4)
- copper salt of 5-hydroxysalicylic acid (Compound Nr. 5)
- 10 • copper salt of 6-hydroxysalicylic acid (Compound Nr. 6)
- copper salt of 3-methylsalicylic acid (Compound Nr. 7)
- copper salt of 4-methoxysalicylic acid (Compound Nr. 8)

Table 1

Compound	R ₁	R ₂	%C (a,c)	%H (a,c)	%Cu (b,c)
1	COCH ₃	H	49.41 (51.2)	3.32 (3.28)	16.04 (15.06)
2	OH	H	46.72 (49.7)	3.21 (2.96)	19.23 (18.81)
3	OH	5-Cl	39.98 (41.31)	2.45 (1.97)	16.56 (15.63)
4	COCH ₃	5-Cl	42.09 (44.01)	2.95 (2.44)	13.51 (12.95)
5	OH	5-OH	42.87 (45.43)	3.15 (2.70)	19.46 (17.18)

6	OH	6-OH	43.67 (45.43)	3.94 (2.70)	18.62 (17.18)
7	OH	3-CH ₃	56.71 (57.59)	3.98 (4.19)	19.79 (19.04)
8	OH	4-OCH ₃	54.36 (52.55)	4.02 (3.83)	16.67 (17.38)

Notes:

- a) values obtained by elemental analysis;
- b) values obtained by gravimetric analysis;
- 5 c) the expected values are indicated in brackets.

EXAMPLE 3

Efficacy of compound Nr. 1 mixed with another fungicidal compound in the control of Venturia inaequalis on apple-tree in preventive leaf application (greenhouse test) Ta-
10 ble 2.

Leaves of wild-type apple-tree, cultivated in vases, in a conditioned environment ($24 \pm 1^\circ\text{C}$, 70% relative humidity) are treated by spraying both sides of the leaves with compound Nr. 1 mixed with another fungicide dispersed in a hydroacetone solution at 20% by volume of acetone containing 0.3% of tween 20.
15

After remaining 48 hours in a conditioned environment, the plants are infected on the lower and higher sides with an aqueous suspension of spores of *Venturia inaequalis* (200,000 spores per cm^3).
20

The plants are kept in a humidity saturated environment, at 21°C, for the incubation period of the fungus and, at the end of this period (14 days), the fungicidal activity is evaluated according to a percentage evaluation scale from 100 (healthy plant) to 0 (completely infected plant).

From the data indicated in Table 2, the synergic effect of the mixtures, consisting of compound Nr. 1 and another fungicide belonging to the various groups cited above, can be observed, compared with the efficacy calculated using the Limpel formula ("Pesticide Science" (1987), vol. 19, pages 309-315:

$$E = x + y - (xy/100)$$

wherein:

- 15 - E is the expected fungicidal activity, without synergic effects, from a mixture obtained by mixing $g \cdot x$ of the compound X with $g \cdot y$ of the compound Y;
- x is the activity of the compound X when used alone at a dose of $g \cdot x$;
- 20 - y is the activity of the compound Y when used alone at a dose of $g \cdot y$;

When the fungicidal activity experimentally evaluated is greater than the value of E, this activity should be considered as a synergic effect.

Table 2

The preventive activity after a day on *Venturia inaequalis* of compound Nr. 1 at 125 ppm (g·x) is 95 (x)

Fungicide	Dosage ppm (g·y)	Activity (y)	Activity of mixture according to Limpel (E)	Experimental mixture activity	Synergy factor
Tetraconazole	60	38	96.9	100	1.03
Difenoconazole	100	36	96.8	97	1.00
Myclobutanil	200	35	96.75	98	1.01
Flusilazole	170	34	96.7	97	1.00
Epoxyconazole	80	30	96.5	97	1.00
Fenpropimorf	300	33	96.65	98	1.01
Fenpropidin	400	37	96.85	99	1.02
Azoxystrobin	0.11	35	96.75	98	1.01
Kresoxym methyl	0.45	35	96.75	98	1.01
Trifloxystrobin	1.8	40	97.0	100	1.03

EXAMPLE 4

Efficacy of compound Nr. 1 mixed with another fungicidal compound in the control of Plasmopara viticola on grapes in preventive leaf application (greenhouse test) Table 3.

Leaves of cultivar Dolcetto grape vines, cultivated in vases, in a conditioned environment ($20 \pm 1^\circ\text{C}$, 70% relative humidity) are treated by spraying both sides of the leaves with compound Nr. 1 mixed with another fungicide dispersed in a hydroacetone solution at 10% by volume of acetone containing 0.3% of tween 20.

After remaining 24 hours in a conditioned environment, the plants are infected on the lower side with an aqueous suspension of spores of *Plasmopara viticola*

(200,000 spores per cm^3).

The plants are kept in a humidity saturated environment, at 21°C , for the incubation period of the fungus and, at the end of this period (7 days), the fungicidal activity is evaluated according to a percentage evaluation scale from 100 (healthy plant) to 0 (completely infected plant).

From the data indicated in Table 3, the synergic effect of the mixtures, consisting of compound Nr. 1 and another fungicide belonging to the various groups cited above, can be observed, compared with the efficacy calculated using the Limpel formula ("Pesticide Science" (1987), vol. 19, pages 309-315:

$$E = x + y - (xy/100)$$

wherein:

- E is the expected fungicidal activity, without synergic effects, from a mixture obtained by mixing $g\cdot x$ of the compound X with $g\cdot y$ of the compound Y;
- x is the activity of the compound X when used alone at a dose of $g\cdot x$;
- y is the activity of the compound Y when used alone at a dose of $g\cdot y$;

When the fungicidal activity experimentally evaluated is greater than the value of E, this activity should be considered as a synergic effect.

Table 3

The preventive activity after a day on Plasmopara viticola of compound Nr. 1 at 30 ppm (g·x) is 53 (x)

5		Fungicide	Dosage ppm (g.y)	Activity (y)	Activity of mixture according to Limpel (E)	Experimental mixture activity	Synergy factor
		Metalaxyl	0.05	34	68.98	77	1.12
		Metalaxyl *	0.05	12	58.64	73	1.24
		Benalaxyl	0.05	42	72.74	84	1.15
		IR 6141	0.025	40	71.8	86	1.20
		Iprovalicarb	0.45	38	70.86	87	1.23
		Ethaboxam	12	33	68.51	77	1.12
10		IR 5885	0.22	39	71.33	87	1.22
		Cyazofamid	4	31	67.57	76	1.12
		Cymozanyl	7.5	34	68.98	74	1.03
		Mancozeb	250	36	69.92	74	1.06
		Clorotalonil	100	32	68.04	76	1.12
		Folpet	50	30	67.1	77	1.15
		Dithianon	37	37	70.39	83	1.18
		Copper hydroxide	150	35	69.45	74	1.07
15		Copper oxychloride	200	34	68.98	73	1.06
		Cuprocalcium oxychloride	250	36	69.92	76	1.09

* Test effected on an isolated portion of the phytopathogen with a reduced sensitivity.

20 EXAMPLE 5

Fungicidal efficacy of compounds having formula (I) in the control of Plasmopara viticola on grapes (field test) Table 4, Table 5 and Table 6.

The efficacy field tests for the control of *Plasmo-*
25 *para viticola* are carried out using an experimental

scheme with randomized blocks which comprise 4 replications and 6-8 plants by repetition.

The grape plants, Barbera variety, are treated by spraying both sides of the leaves either with a compound
5 having formula (I) or with a mixture containing one or more salts having formula (I) and another fungicide, object of the present invention, formulated as wettable powder WP50.

The tests are carried out by treatment at a fixed
10 period of 7 days for the mixtures of a compound of formula (I) with IR6141 and at a fixed period of 10 days for the mixtures of a compound of formula (I) with IR 5885.

The measurements, made when the presence of the pathogen is observed on the non-treated blank plot, are
15 effected on both the leaves and the cluster.

The measurement on the leaves is effected by counting 100 grape leaves per plot (total 400 leaves) and marking the leaf surface percentage struck by the disease.

20 The measurement on the clusters, on the other hand, is effected by analyzing all the clusters and considering the percentage of surface damaged.

The data relating to the field tests of compounds Nr. 2-4 compared with Mancozeb and copper oxychloride,
25 are provided in Table 4.

Table 4

Product	Dosage gpa/hl	Leaf disease % reduction	Cluster disease % reduction
Blank		100 *	98.86 *
Compound nr.2	128	89.47	91.52
Compound nr.3	150	90.40	92.00
Compound nr.4	50	90.10	90.80
Copper Oxychloride	800	82.00	87.02
Mancozeb	2000	88.50	88.50

(gpa/hl) = grams of active principle per hectoliter

* = incidence of the disease.

The data relating to the field tests of compounds Nr. 1-4, mixed with IR6141 are provided in Table 5, the data relating to the field tests of compounds Nr. 1, 2, 4 and 8, mixed with IR5885 are provided in Table 6.

Table 5

Product	Dosage gpa/hl	Leaf disease % reduction	Cluster disease % reduction
Blank		99 *	95 *
Compound nr.1 + IR 6141	80 + 10	97	94
Compound nr.2 + IR 6141	80 + 10	96	94
Compound nr.3 + IR 6141	85 + 10	99	97
Compound nr.4 + IR 6141	40 + 10	95	95
IR 6141 + Copper hydroxide	10 + 110	93	90

(gpa/hl) = grams of active principle per hectoliter

* = incidence of the disease.

Table 6

Product	Dosage gpa/hl	Leaf disease % reduction	Cluster disease % reduction
Blank		99 *	95 *
Compound nr.1 + IR 5885	100 + 12	99	98
Compound nr.2 + IR 5885	100 + 12	98	97
Compound nr.4 + IR 5885	40 + 12	99	98
Compound nr.8 + IR 5885	100 + 12	97	96

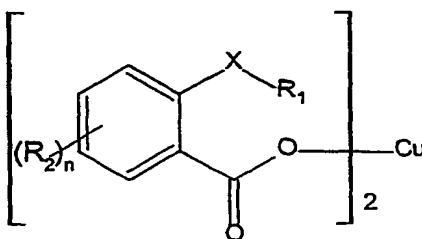
(gpa/hl) = grams of active principle per hectoliter

5 * = incidence of the disease.

CLAIMS

1. Fungicidal compositions containing one or more salts of salts of derivatives of salicylic acid having formula (I):

5



10

(I)

wherein:

- R_1 represents H, or a $\text{CO}-\text{R}'$ acyl group;
- R_2 , the same or different when n is equal to 2, is a hydrogen, a halogen, optionally selected from fluorine, chlorine, bromine or iodine; a C_1-C_9 alkyl group; a C_1-C_9 haloalkyl group; a C_1-C_9 alkoxy group; a C_1-C_9 haloalkoxy group; a C_1-C_9 thioalkyl group; a C_1-C_9 halothioalkyl group; a C_3-C_9 cycloalkyl group; a C_2-C_{10} carboalkoxy group; a cyano group; a phenyl group; a hydroxyl group;
- R' represents a hydrogen; a C_1-C_9 alkyl group; a C_1-C_9 haloalkyl group; a C_1-C_9 alkoxy group; a C_1-C_9 haloalkoxy group; a C_2-C_{10} carboalkoxy group; a phenyl group;
- n is a number ranging from 0 to 2;

- X represents an oxygen atom, a nitrogen or sulfur atom;

in any molar ratio, with at least one fungicidal compound not corresponding to a salt of derivatives of salicylic acid having formula (I).

2. The compositions according to claim 1, characterized in that the fungicidal compound not corresponding to a salt of derivatives of salicylic acid having formula (I) is selected from inhibitors of ergosterol biosynthesis, inhibitors of mitochondrial respiration, acylanilines, systemic anti-mildew fungicides, a dipeptide with a fungicidal activity, cytotropic anti-mildew fungicides, contact fungicides, cupric fungicides, inhibitor fungicides of melanin biosynthesis.

3. The compositions according to claim 1, characterized in that the fungicidal compound not corresponding to a salt of derivatives of salicylic acid having formula (I) can be selected from tetraconazole, difenoconazole, myclobutanil, flusilazole, epoxyconazole, fenpropimorf, fenpropidin, azoxystrobin, kresoxym methyl, trifloxystrobin, metalaxyl, benalaxyl in its racemic form or as an optically active R isomer (called IR 6141), iprovalicarb, ethaboxam, cyazofamid, cymoxanil, mancozeb, clorotalonil, folpet, ditianon, copper hydroxide, copper oxychloride, cuprocalcium oxychloride.

4. The compositions according to claim 1, characterized in that the compounds having formula (I) are present in hydrated form by the coordination of any number of water molecules.

5 5. The compositions according to claim 1, characterized in that, in the compounds having formula (I), R_2 is selected from fluorine, chlorine, methyl, trifluoromethyl, hydroxyl.

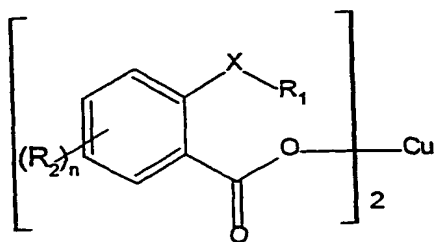
6. The compositions according to claim 1, characterized
10 in that they are formulated as dry powders, wettable powders, emulsifiable concentrates, micro-emulsions, pastes, granulates, solutions, suspensions, etc.

7. The compositions according to claim 1, characterized in that they contain additives such as adhesion agents,
15 such as gum arabic, polyvinyl alcohol, polyvinylpyrrolidone, polyacrylates and/or other compatible active principles such as phyto regulators, antibiotics, herbicides, insecticides, fertilizers.

8. The compositions according to claim 1, characterized
20 in that the concentration of the active substances ranges from 0.1% to 98%, preferably from 0.5% to 90%.

9. Salts of derivatives of salicylic acid having formula (I):

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(I)

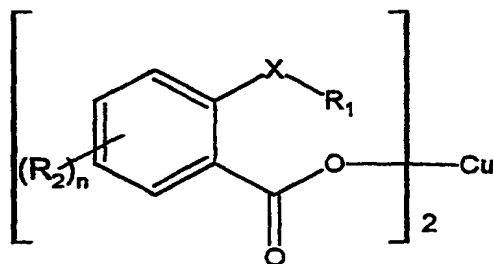
wherein:

- 10 - R_1 represents H, or a CO-R' acyl group;
- R_2 , the same or different when n is equal to 2, is a halogen, optionally selected from fluorine, chlorine, bromine or iodine; a $\text{C}_1\text{-C}_9$ alkyl group; a $\text{C}_1\text{-C}_9$ haloalkyl group; a $\text{C}_1\text{-C}_9$ alkoxy group; a $\text{C}_1\text{-C}_9$ haloalkoxy group; a $\text{C}_1\text{-C}_9$ thioalkyl group; a $\text{C}_1\text{-C}_9$ halothioalkyl group; a $\text{C}_3\text{-C}_9$ cycloalkyl group; a $\text{C}_2\text{-C}_{10}$ carboalkoxy group; a cyano group; a phenyl group; a hydroxyl group;
- 15 - R' represents an alkyl group, optionally selected from methyl, propyl, isopropyl; or the haloalkyl group trifluoromethyl; or hydrogen;
- 20 - n is a number ranging from 0 to 2;
- X represents an oxygen atom, a nitrogen or a sulfur atom;
- 25 with the exception, when X is equal to oxygen, of com-

pounds wherein R_1 represents the acyl group COCH_3 and R_2 is hydrogen or chlorine and compounds wherein R_1 represents the acyl group COiPr or COEt and R_2 is hydrogen.

10. The salts according to claim 9, characterized in that the compounds having formula (I) are present in hydrated form by the coordination of any number of water molecules.

11. Use of fungicidal compositions containing one or more salts of derivatives of salicylic acid having formula (I):



(I)

wherein:

- R_1 represents H, or a $\text{CO}-\text{R}'$ acyl group;
- R_2 , the same or different when n is equal to 2, is a hydrogen, a halogen, optionally selected from fluorine, chlorine, bromine or iodine; a C_1-C_9 alkyl group; a C_1-C_9 haloalkyl group; a C_1-C_9 alkoxy group; a C_1-C_9 haloalkoxy group; a C_1-C_9 thioalkyl group; a C_1-C_9 halothioalkyl group; a C_3-C_9 cycloalkyl group; a C_2-C_{10} carboalkoxy group; a cyano group; a phenyl group; a

hydroxyl group;

- R' represents a hydrogen; a C₁-C₉ alkyl group; a C₁-C₉ haloalkyl group; a C₁-C₉ alkoxy group; a C₁-C₉ haloalkoxy group; a C₂-C₁₀ carboalkoxy group; a phenyl group;

- n is a number ranging from 0 to 2;

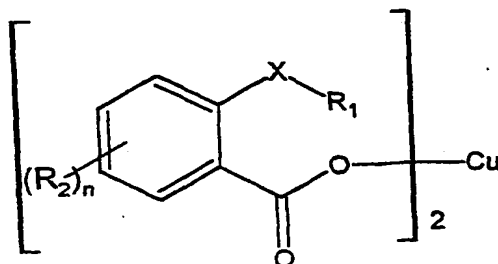
- X represents an oxygen atom, a nitrogen or a sulfur atom;

in any molar ratio, with at least one fungicidal compound not corresponding to a salt of derivatives of salicylic acid having formula (I),

for the control of phytopathogens on vegetables or parts thereof.

12. Use of fungicidal compositions according to any of the claims from 2 to 8 for the control of phytopathogens on vegetables or parts thereof.

13. Use of salts of derivatives of salicylic acid having formula (I):



(I)

25 wherein:

- R₁ represents H, or a CO-R' acyl group;
 - R₂, the same or different when n is equal to 2, is a halogen, optionally selected from fluorine, chlorine, bromine or iodine; a C₁-C₉ alkyl group; a C₁-C₉ haloalkyl group; a C₁-C₉ alkoxy group; a C₁-C₉ haloalkoxy group; a C₁-C₉ thioalkyl group; a C₁-C₉ halothioalkyl group; a C₃-C₉ cycloalkyl group; a C₂-C₁₀ carboalkoxy group; a cyano group; a phenyl group; a hydroxyl group;
 - 10 - R' represents an alkyl group, optionally selected from methyl, propyl, isopropyl; or the haloalkyl group trifluoromethyl; or hydrogen;
 - n is a number ranging from 0 to 2;
 - X represents an oxygen atom, a nitrogen or a sulfur atom;
- 15 for the control of phytopathogens on vegetables or parts thereof.
14. Use of the salts according to claim 10 for the control of phytopathogens on vegetables or parts thereof.
- 20 15. Use according to one of the claims from 11 to 14 for the control of bacterial and fungal phytopathogens.
16. Use according to one of the claims from 11 to 14 for the control of phytopathogens which have become tolerant to a fungicidal compound not corresponding to a salt of
- 25 derivatives of salicylic acid having formula (I).

17. Use according to one of the claims from 11 to 14 on genetically modified vegetable varieties.

18. Use according to one of the claims from 11 to 14 in vegetable varieties also genetically modified, for amplifying the defense systems of the plants.

19. Use according to claim 17, in genetically modified vegetable varieties in which one or more genes expressing fungicidal proteins have been inserted, in response to variations in the content of the same salicylic acid in the tissues.

20. Use according to one of the claims from 11 to 19, characterized in that the phytopathogens controlled are *Plasmopara viticola* on grapes, *Peronospora tabacina* on tobacco, *Venturia inaequalis* on apple-trees, *Bremia* on salads, spinach, *Phytophthora* spp. on vegetables, *Pseudoperonospora cubensis* on cucurbitaceae, *Pyricularia orizae* on rice.

21. A method for fighting fungal infections consisting in applying the fungicidal compositions according to claim 1-8, on plants, leaves, stems, branches and roots, or on the seeds themselves before sowing, or on the ground in which the plant grows.

22. A method for fighting fungal infections consisting in applying the salts according to claims 9 and 10, on plants, leaves, stems, branches and roots, or on the

seeds themselves before sowing, or on the ground in which
the plant grows.

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INTERNATIONAL SEARCH REPORT

 Int. Application No
 PCT/EP 02/12982

A. CLASSIFICATION OF SUBJECT MATTER

 IPC 7 C07C65/05 C07C65/21 C07C69/017 A01N59/20 A01N37/36
 A01N37/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 15189 A (BASF AG ;HAMPEL MANFRED (DE); SCHELBERGER KLAUS (DE); LORENZ GISEL) 1 May 1997 (1997-05-01) page 1 page 2, line 12-16 page 2, line 26 -page 3, line 6 page 3, line 39 -page 4, line 7 claims 1,2,9	1,2,6-9, 11-15, 20-22
X	US 5 756 524 A (OSBOURN SUSAN ELIZABETH ET AL) 26 May 1998 (1998-05-26) abstract column 3, line 5-32 claims 1,8,17	1,2,6-9, 11-13, 15,20-22



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

4 April 2003

Date of mailing of the international search report

17/04/2003

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DeLanghe, P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12982

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 995 034 A (STROBEL ALBERT F) 30 November 1976 (1976-11-30) abstract column 3, line 8-12 claims 1-3 ----	9,13,15, 22
X	EP 0 453 922 A (BAYER AG) 30 October 1991 (1991-10-30) page 2, line 1 -page 5, line 10 example 1 ----	1,9,13
X	FR 2 140 269 A (ARIES ROBERT) 19 January 1973 (1973-01-19) page 2, line 13 -page 3, line 8 ----	1,9,13
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; JHA, RAJ RANJAN ET AL: "Structure and derivatographic study of 3d-series transition metal complexes with salicylic acid" retrieved from STN Database accession no. 107:210893 XP002233438 abstract & CHIMICA ACTA TURCICA (1986), 14(1), 51-63 , ----	9,10
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LUCANSKA, B. ET AL: "Antiinflammatory activity of aqua(dihydroxybenzoato)copper(II) complexes" retrieved from STN Database accession no. 116:98099 XP002233437 abstract & CONFERENCE ON COORDINATION CHEMISTRY (1991), 13TH, 155-60 , ----- -/-	9,10

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12982

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MICERA, G. ET AL: "Interaction of metal-ions with humic-like models. Part 8. Manganese(II) cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 2,4-dihydroxybenzoic acid" retrieved from STN Database accession no. 104:14039 XP002233439 abstract & INORGANICA CHIMICA ACTA (1985), 108(1), L1-L2 ,</p>	9,10
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SOKOLIK, JOZEF ET AL: "Anti-inflammatory and antipyretic activities of the aqua(dihydroxybenzoato)copper(II) complexes" retrieved from STN Database accession no. 117:204558 XP002233440 abstract & CESKO-SLOVENSKA FARMACIE (1992), 41(4-5), 127-9 ,</p>	9,10
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; CARIATI, F. ET AL: "Interaction of metal ions with humiclike models. Part I. Synthesis, spectroscopic and structural properties of diaquabis(2,6- dihydroxybenzoato)copper(II) and hexaaquaM(II) bis(2,6-dihydroxybenzoate) dihydrate (M = Mn, Fe, Co, Ni, Cu and Zn)" retrieved from STN Database accession no. 99:114939 XP002233441 abstract & INORGANICA CHIMICA ACTA (1983), 80(1-2), 57-65 ,</p>	9,10

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INTERNATIONAL SEARCH REPORT

Int. Patent Application No

PCT/EP 02/12982

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HULKOVA, O. ET AL: "EPR and electronic spectra of cresotatoaquocopper(II) complexes" retrieved from STN Database accession no. 76:92755 XP002233442 abstract & PROC. CONF. COORD. CHEM., 3RD (1971), 115-20. EDITOR(S): GAZO, JAN. PUBLISHER: SLOVAK TECH. UNIV, BRATISLAVA, CZECH. ,</p>	9,10
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MELNIK, MILAN ET AL: "Crystal structure, spectral and magnetic behavior of copper(II)(5- chlorosalicylato)2(aqua)2" retrieved from STN Database accession no. 136:78871 XP002233443 abstract & JOURNAL OF COORDINATION CHEMISTRY (2001), 53(2), 173-179 ,</p>	9,10
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SOKOLIK, JOZEF ET AL: "Anti-inflammatory and antipyretic activities of the aqua(dihydroxybenzoato)copper(II) complexes" retrieved from STN Database accession no. 117:204558 XP002233445 abstract & CESKO-SLOVENSKA FARMACIE (1992), 41(4-5), 127-9 ,</p>	9,10
X	<p>DATABASE WPI Section Ch, Week 198022 Derwent Publications Ltd., London, GB; Class D22, AN 1980-39596C XP002233446 & SU 690 166 A (BASHKIR PETROL IND), 5 October 1979 (1979-10-05) abstract</p>	9

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12982

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LIU, ZIRU ET AL: "Thermal Decomposition of cupric benzoate and its derivatives. (II). Mechanism of thermal decomposition of cupric benzoates with two substituents" retrieved from STN Database accession no. 127:348500 XP002233444 abstract & GUTI HUOJIAN JISHU (1997), 20(3), 49-52</p>	9
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; VERRALL, A. F. ET AL: "Preservative treatments for protecting wood boxes" retrieved from STN Database accession no. 71:60008 XP002233436 abstract & RESEARCH PAPER FPL - FOREST PRODUCTS LABORATORY (UNITED STATES) (1969), FPL-106, 8 PP. ,</p>	9
P,X	<p>WO 02 39963 A (ZEILER KENNETH T) 23 May 2002 (2002-05-23) page 2, line 11-26 page 4, line 1-6 claims 17,18</p>	9,13,20
A	<p>DD 299 034 A (FAHLBERG LIST VEB) 26 March 1992 (1992-03-26) the whole document</p>	1,9,11, 13,21

INTERNATIONAL SEARCH REPORT

national application No.
PCT/EP 02/12982

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-22 (partially)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-22 (partially)

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim(s) may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claim(s) is impossible. Consequently, the search has been restricted to compounds of formula 1 in claim 9 and the hydrated forms of these salts.

The composition claims 1-8 have been similarly limited.
The use claims 11-22 have been similarly limited.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Initial International Application No

PCT/EP 02/12982

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